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RADIOACTIVE ISOTOPES OF THE RARE EARTH ELEMENTS III. LUTECIUM ISOTOPES AND HAFNIUM ISOTOPES

By Geoffrey Wilkinson Harry G. Hicks

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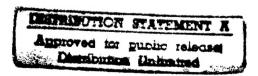
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PRINTED IN USA REFICE 10 CENTS Radioactive Isotopes of the Rare Earth Elements
III Lutecium Isotopes and Hafnium Isotopes*

Geoffrey Wilkinson and Harry G. Hicks Radiation Laboratory and Department of Chemistry University of California, Berkeley, California

ABSTRACT

A study has been made of radioactive isotopes of lutecium and hafnium, produced by bombardments of thulium and ytterbium with 38, 31, and 19 Mev & particles, of lutecium and hafnium with 19 Mev deuterons, and of tantalum with 190 Mev deuterons.

^{*}Work performed under Contract No. W-7405-eng-48

Radioactive Isotopes of the Rare Earth Elements

III Lutecium Isotopes and Hafnium Isotopes

Geoffrey Wilkinson and Harry G. Hicks Radiation Laboratory and Department of Chemistry University of California, Berkeley, California

I. Introduction

The techniques of bombardments, chemical separations, measurement of radioactivities, etc., used have been described previously (1). These have now been applied

(1) G. Wilkinson, H. G. Hicks, Phys. Rev. 75, 1370 (1949).

to a study of radioactive isotopes of lutecium, and, since the interpretation of data has depended upon the characterization of lutecium daughters of hafnium parents, also of radioactive isotopes of hafnium. The present knowledge of radioactive isotopes of these elements is given in Table I.

Using the 60-inch Crocker Laboratory cyclotron, bombardments have been made of thulium with various energies of helium ions, of ytterbium with 10 Mev protons, and of lutecium with 19 Mev deuterons and fast neutrons from a <u>Be + d</u> source. Ytterbium has also been bombarded with 38 and 19 Mev a-particles, and lutecium activities produced by growth in the chemically separated hafnium fraction isolated and studied. Lutecium activities were also produced in the bombardment of hafnium with 19 Mev deuterons and in the bombardment of tantalum with 200 Mev deuterons from the 184-inch cyclotron.

After bombardments, the rare earth oxides were dissolved in boiling nitric acid, and the rare earth purified by repeated fluoride-hydroxide precipitation cycles. The individual rare earths were then separated by the ion exchange resin column method. The hafnium oxide was dissolved by fusion with potassium bisulphate. The cold melt was dissolved in water and the hydroxide recovered by ammonia precipitation.

After addition of carriers the rare earth fraction was separated by fluoride precipitation. Hafnium was recovered by precipitation of barium hafnium fluoride. (2)

(2) G. Wilkinson, H. G. Hicks, Phys. Rev. 75, 696 (1949).

Table I
Radioactive Isotopes of Lutecium and Hafnium

Isotope	Type of Radiation	Half-Life	Energy of Radiat Particles	tion in Mev Y-rays	Produced by
Lu ¹⁷⁰	Κ,e ⁻ ,Υ	2.1 ⁺ 0.1 days	0.1	L,K x-rays ~2.5	Tm-α-3n Ta-d-3z13a
Lu ¹⁷¹	К,е¯,Υ	8.5 ⁺ 0.2 days	0.17,~0.5	L, Kx-rays	Tm-α-2n Ta-α-3z12a
Lu ¹⁷²	K,e¯,Υ	500 ± 20 days	~0.1,~0.16	L,Kx-rays	Ta-α-n Ta-d-Z ^{3z} lla Hf K decay
Lu ¹⁷²	β ⁺	4.0 ± 0.1 hours	1.2		Tm-α-n Yb-p-n
Lu ¹⁷²	k,β ⁺ (~20%)	3.40 ± 0.05 days	1.8	Kx-rays	Tm-c-n Yb ī P zn Hf ⁷² K decay
Lu ¹⁷³	Κ, e ⁻ ,Υ	6.7 [±] 0.1 days	0.13,~0.6	L, Kx-rays	Hf ¹⁷² K decay Yb-p-n
Lu ¹⁷⁴	K,e ⁻ ,Υ β-(~25%)	160 [±] 5 days	0.16(e¯) 0.6(β¯)	L, Kx-rays	Lu-n-2n Hf-d-a Lu-d-p2n
Hf ^{172,3}	Κ, Θ , Υ?	22.0 ± 0.5 hours	0.12 0.22	L,Kx-rays	Yb-α-2n,3n
Hf ¹⁷³	Κ,e¯,Υ? .	~5 years	No e	L, Kx-rays	Yb-a-n,2n,3n Ta-d-2z10a

II. Lutecium Isotopes

The bombardment of thulium with α -particles of various energies enabled the characterization of five radioactive isotopes of lutecium to be made. These were isotopes of half lives 4.0 hours, 2.1 days, 3.4 days, 8.5 days and 500 days. From

short bombardments at 38 MeV, the 2.1 day and 8.5 day activities were readily resolved. In longer bombardments at 38 MeV, the 4.0 hour and 3.4 day activities were seen in low yields and were recognized from their positron emission using a simple beta ray spectrograph; although the 4.0 hour activity was observed in decay of electron and electromagnetic radiation, the 3.4 day activity was masked by the 8.5 day activities was possible though difficult; with 19 MeV a-particles, the 4.0 hour and 3.4 day lutecium activities were readily resolvable although the 8.5 day activity was present in low yield. The 500 day activity was found in all samples. From the yields in bombardments and from other considerations discussed subsequently, the 2.1 day and 8.5 day activities are allocated to masses 170 and 171, while the 4.0 hour, 3.4 day and 500 day activities are all allocated to mass 172.

The resolution of decay and absorption curves of the lutecium activities produced in proton bombardments of ytterbium has proved very difficult; the 4.0 hour and 3.4 day activities were recognized only through their positron emissions. The 2.1 day activity was not apparent, as would be expected from its allocation to mass 171, since Yb¹⁷¹ has an abundance of only 4.21%. The decay and absorption curves of the longer lived activities were almost impossible to resolve; these are now known to consist of the 8.5 day and 500 day activities together with activities of half-lives 6.7 days and 160 days allocated respectively to masses 173 and 174.

Fast neutron and deuteron bombardments of lutecium have led to the establishment of a 160 day Lu¹⁷⁴ activity decaying by both orbital electron capture and negative beta particle emission.

The production of hafnium activities by a-particle bombardments of ytterbium, and from spallation reactions of 200 Mev deuterons in tantalum has allowed the isolation of 3.4 day and 6.7 day lutecium daughter activities, and has allowed the radiation characteristics of these activities to be determined much more readily than by resolution of complex decay and absorption curves from Tm + a and Yb + p bombardments.

3.75 hour Lu¹⁷⁶ 6.70 day Lu¹⁷⁷

In bombardments of lutecium with neutrons and deuterons, and in the bombardment of hafnium with 19 Mev deuterons, both these well known (3) beta emitting isotopes

(3) G. T. Seaborg, I. Perlman, Rev. Mod. Phys, 20, 585 (1948).

have been observed. Measurement of the beta activities from deuteron bombardments of lutecium allowed unequivocal allocation of the 3.75 hour and 6.70 day activities to masses 176 and 177 on the basis of cross sections for the d.p reaction. For natural lutecium the cross sections for the 3.75 and 6.7 day activities were respectively 4.3×10^{-2} and 0.1×10^{-3} barns, which give isotopic cross sections for d.p reactions in Lu¹⁷⁵ and Lu¹⁷⁶ of 4.4×10^{-2} and 4.0×10^{-2} barns respectively.

The half lives of the two activities as measured were 3.75 ± 0.05 hours through nine half-lives and 6.70 ± 0.05 days through ten half-lives. The radiation characteristics obtained agree with those observed by other workers.

160 day Lu¹⁷⁴

A long-lived activity has been found in the ion exchange column separated lutecium fractions from lutecium bombarded with 19 Mev deuterons, and with fast neutrons from both cyclotron and pile bombardments; it has also been found together with the 6.70 day Lu¹⁷⁷ in the lutecium fraction from hafnium bombarded with 19 Mev deuterons. Allocation can be therefore made to Lu¹⁷⁴ on the basis of formation by Lu-n-2n, Lu-d-p2n and Hf-d-a reactions. The cross section for the d,p2n reaction in lutecium of approximately 5 x 10⁻⁴ barns was calculated from ratios of the beta activities of the 6.70 day Lu¹⁷⁶ formed by Lu¹⁷⁵-d-p reaction and the 160 day Lu¹⁷⁴. The half life measured through three periods is 160 ± 5 days. Absorption measurements (Fig. I) show electrons ranges 30 mg/cm² (0.16 Mev) and ~180 mg/cm² aluminum, with electromagnetic radiations of half thicknesses 14 mg/cm² aluminum (8 Kev) and 100 mg/cm² lead (55 Kev);

harder gamma radiation in low intensity was found in the samples to an extent of about 10% of the K x-radiation. The ratios of the various radiations obtained making previously discussed (1) assumptions regarding counting efficiencies etc., were

0.16 Mev e : 0.6 Mev e : L x-rays : K x-rays : Υ-rays NO.7 ~0.2 : ~1.5 :

From the energy, and type of absorption curve, it seems that the harder electron is a negative beta-particle. The L and K x-radiation seems to be too abundant for any scheme of disintegration by isomeric transitions and the isotope thus probably decays by both beta-emission and by orbital electron capture, the latter accounting for possibly 75% of the disintegrations.

2.1 ± 0.1 day Lu¹⁷⁰

In the bombardment of thulium with 38 Mev a-particles only, an activity of 2.1 days half-life was observed (Fig. II). The decay of electron and electromagnetic radiations were followed separately through about eight periods to give a value of 2.1 $\stackrel{+}{=}$ 0.1 days for the half-life. The radiation characteristics obtained from resolution of decays and beryllium, aluminum and lead absorption measurements (Fig. III) consist of electrons, total range 14 mg/cm² aluminum (0.1 Mev) with electromagnetic radiation of half-thicknesses 14 mg/cm² aluminum (8 Kev), ~95 mg/cm² lead (~52 Kev) and ~16.5 g/cm2 lead (~2.5 Mev). No positrons associated with the 2.1 day activity were observed on a simple beta ray spectrograph. The approximate ratios of the various radiations corrected for counting efficiencies, etc. as discussed previously, were

O.1 Mev e : L x-rays : K x-rays : ~2.5 Mev Y ray

~0.3 : ~0.2 :

8.5 ⁺ 0.2 day Lu¹⁷¹

In bombardments of thulium with 38 and 31 Mev a-particles an activity of half-life 8.5 - 0.2 day, measured through seven half lives, was observed (Fig. III). The variation of yield with bombarding energy allows fairly certain allocation to mass 171, and production of the activity by <u>Tm-o-2n</u> reaction. The radiation characteristics obtained by resolution of decay and absorption curves (Fig. IV), consist of electrons total ranges 35 mg/cm² (0.17 MeV) and ~150 mg/cm² (~0.5 MeV), with electromagnetic radiation of half thicknesses~14 mg/cm² aluminum (8 KeV) and ~100 mg/cm² lead (55 KeV). No positrons were observed in the radiations. The ratios of the various radiations were

0.17 Mev e : 0.5 Mev e : L x-rays : K x-rays

~0.05 : ~0.005 : ~0.1 : 1

500 ± 20 day Lu¹⁷²

In all bombardments, but in particularly high yield in bombardment of thulium with 19 Mev a-particles, a very long lived activity was observed after decay of shorter lived activities; allocation of this activity to mass 172 is discussed subsequently. The radiations (Fig. V) comprise electrons, total ranges~14 mg/cm² (~0.1 Mev) and ~30 mg/cm² (~0.16 Mev), with the usual L and K x-radiation.

The activity, the best half life for which at present is 500 ± 20 days, has been also found in lutecium fractions from bombardment of tantalum with 200 Mev deuterons; the radiation characteristics were identical in all respects with those obtained for the activity from $\underline{\text{Tm}} + \alpha$ bombardments.

4.0 ⁺ 0.1 hour Lu¹⁷²

In bombardments of thulium with α -particles of energies 38, 31, and 19 Mev, a positron emitting activity of 4 hours half-life has been observed. The absorption characteristics and decays in all cases were the same. Fig. VI shows the decay from a 19 Nev bombardment; the half-life measured through eight periods is 4.0 ± 0.1 hours. The aluminum absorption corrected for decay during time of measurement, and for the small contribution from longer-lived activity is shown in Fig. VI. The hard radiation, range 500 mg/cm² aluminum (1.2 Mev) was shown on a simple beta ray spectrograph to consist of positrons. No negative electrons were observed.

Sufficient activity was not available for measurement of a lead absorption, but from the aluminum absorption curve, assuming 0.5% counting efficiency for the hard

electromagnetic radiation background, the ratio of positrons to γ quanta is 1:2. It seems probable therefore that the 4 hour activity decays mainly by positron emission and that the γ -radiation is annihilation radiation.

The activity has been allocated to mass 172 on the basis of yields at the three energies of a-particles used, and its formation by <u>Tm-a-n</u> reaction seems certain. The cross sections at 38, 31 and 19 Mev for the 4 hour activity are given subsequently.

3.40 ± 0.05 day Lu¹⁷²

In 19 Mev a-particle bombardments of thulium, an activity of 3.4 days half-life was observed; in bombardments at higher energies this activity was masked by the 8.5 day activity which was formed in much higher yields. The activity has been obtained free from all but the 500 day isotope, which was present in very low yield, by chemical separation of lutecium daughter activities in the hafnium fraction from bombardment of ytterbium with a-particles. The radiation characteristics (Fig. VII) of the activity from both sources are the same, and consist of positrons range ~850 mg/cm² (1.8 MeV) with electromagnetic radiation background of initial half thickness ~2400 mg/cm² aluminum (~53 MeV) suggesting presence of K x-radiation of ytterbium or lutecium. A lead absorption of electromagnetic radiation was not made due to lack of sufficient activity. The ratio of positron to electromagnetic radiations in many samples of the 3.4 day activity milked from hafnium was constant and assuming 0.5% counting efficiency for the electromagnetic radiation was 0.17. This suggests that the isotope decays by both positron emission and orbital electron capture, the former to the extent of about twenty percent.

In the $\underline{\text{Tm}} + \underline{\alpha}$ bombardments the decay of the 3.4 day activity (Fig. VIII) was followed through about six half-lives, and the decays of samples of the separated lutecium daughter activity were followed through eleven half-lives, to give a value of 3.40 $^{+}$ 0.05 days for the half-life.

In the bombardment of ytterbium with protons, the separated lutecium fraction studied on a simple beta ray spectrograph shows the presence of positrons decaying

with a 3.4 day half-life. The 3.4 day activity could not be resolved in gross decays due to the presence of other activities.

6.7 + 0.1 day Lu¹⁷³

The decays of column separated lutecium fractions from 10 Mev proton bombardments of ytterbium had a half-life of about seven days noticeably less than the half-life of the 8.5 day Lu¹⁷¹ activity produced by a-particle bombardment of thulium. Since Yb¹⁷¹ and Yb¹⁷³ have similar abundances, lutecium activities of these masses would be very difficult to resolve if the half-lives were similar, and the resolution of the separated lutecium fractions is indeed virtually impossible by methods using decay and absorption measurements.

From a long bombardment of tantalum with 200 Mev deuterons a hafnium activity of about five years half-life has been isolated. This activity has been found to grow a lutecium daughter of half-life 6.7 ± 0.1 days followed through ten half-lives (Fig. X). The 5 year hafnium has been observed in present α-particle bombardments of ytterbium only in very low yields. The radiation characteristics of the 6.7 day activity (Fig. IX) comprise electrons total ranges ~23 mg/cm² (~0.13 Mev) and ~200 mg/cm² (~0.6 Mev), electromagnetic radiations of half thickness 14 mg/cm² aluminum (8 Kev), together with harder K x-ray or γ-ray radiation. Assuming a counting efficiency of 0.5% for the hard electromagnetic radiation, the ratios of the various radiations are approximately

0.13 Mev e : 0.6 Mev e : L x-rays : K + Y rays ~0.1 : ~0.007 : ~0.1

III. Hafnium Isotopes 5 Year Hf¹⁷¹

In the hafnium fractions from both α-particle bombardments of ytterbium and 200 Mev deuteron bombardments of tantalum, a very long lived activity remains after decay of shorter lived isotopes. Sufficient activity has not been available for measurement of lead absorption of gamma radiation, but the absorption of softer

components in beryllium and aluminum has been measured (Fig. XI) showing the presence of electromagnetic radiation only, corresponding to L and K x-radiation. From both chemical separations and activity measurements (Fig. X), the hafnium activity has been shown to grow only the 6.7 day lutecium activity allocated to mass 171.

22.0 + 0.5 hour Hf¹⁷² or 173

The hafnium fraction from both 38 and 19 Mev a-particle bombardments of ytterbium decays initially with a 22.0 hour half-life. Chemical separation of lutecium from hafnium during this time showed no evidence for the formation of any daughter activity. The 22.0 hour isotope could possibly be a parent of the 500 day lutecium activity but no evidence for such a relationship could be obtained with the intensities available. The decay followed through eight periods gave 22.0 $^{+}$ 0.5 hours for the half-life; absorption measurements (Fig. XII) show electrons total ranges 20 and 55 mg/cm² (0.12 Mev and 0.22 Mev) with electromagnetic radiations half thickness ~15 mg/cm² (8 Kev) and harder components.

>50 day Hf 172

Indirect evidence only has been obtained for the existence of this isotope. Chemical separation of lutecium from the hafnium fractions from a particle bombardments of ytterbium show the growth of the 3.4 day lutecium activity from a hafnium parent of long life. The presence of the 67 day Hf¹⁷⁵ in high yields in all bombardments would mask the decay of an isotope of similar half-life, and it proved impossible to resolve the decay and absorption data for the hafnium fractions to show the parent of the 3.4 day lutecium activity.

Discussion

In Table II are given the yields of the various lutecium isotopes formed in the a-particle bombardments of thulium; the yield of the most abundant activity at a given bombarding energy is taken as unity.

Table II

38 Me v	31 Mev	19 Mev	Probable Reaction
0.5	*** *** ·	· •• •• ••	a3n
1	. 1	< 0.01	o2n
0.3	1	1	œ
0.01	0.02	~ 0.02	œ
to == 40		0.03	co n
	0.5 1 0.3 0.01	0.5 1 1 0.3 1 0.01 0.02	0.5 1 1 < 0.01 0.3 1 1 0.01 0.02 ~ 0.02

While the allocation of the 2.1 day activity to Lu¹⁷⁰ is fairly certain, the cross section for production of the isotopes at 38 MeV is however only about 0.01 barns, a value much lower than those obtained for yields of a.3n reactions with other elements in this region. It is probable therefore that an activity of short half-life isomeric with the 2.1 day activity exists; in the present work, an activity of half-life greater than about five minutes would have been observed. The present allocation is confirmed by absence of the 2.1 day activity in lutecium fractions from a particle bombardments of ytterbium, from which it could be formed only by a.pn reaction on the Yb¹⁶⁸ (0.06% abundance) or by decay from Hf¹⁷⁰ produced by a.2n reaction on Yb¹⁶⁸. It has also not been found in proton bombardments of ytterbium where it would be formed in low yield by Yb¹⁷⁶-p-n reaction.

The allocation of the 8.5 day activity to Lu^{171} from yields in $\underline{Tm + \alpha}$ bombardment is confirmed by its absence in lutecium fractions from Yb + α bombardments

where the isotope would be formed directly by $\underline{a_3p2n}$ reactions on $Yb^{170}(4.21\%$ abundance) or indirectly from Hf^{171} which could arise only in low yield from $\underline{a_33n}$ reaction in Yb^{170} .

23

The yields of the 500 day activity in $\underline{\text{Tm}} + \underline{\alpha}$ bombardments require allocation to mass 172, although a possibility exists that the isotope could be of mass 171. However, evidence has been obtained for growth of the 500 day lutecium from hafnium activities formed in bombardment of ytterbium with both 38 and 19 Mev α -particles; this eliminates mass 171 as a possibility since Hf^{171} could be formed only by α ,3n reaction with the low abundant Yb¹⁷⁰. The 500 day activity must of necessity be placed at mass 172.

The 3.4 day positron emitting activity was observed only in the 19 Mev a-bombardments of thulium indicating formation by a,n reaction; its growth from a long lived hafnium formed in high yields in both 38 and 19 Mev a-particle bombardments of ytterbium limits the possibilities for allocation to mass 172 only.

The 4.0 hour positron emitter was observed in all $\underline{\text{Im}} + \underline{\alpha}$ bombardments, but in highest yield in the 19 Hev bombardments indicating formation by $\underline{\alpha}$,n reaction. The activity was found in lutecium fractions from proton and α -particle bombardments of ytterbium; formation in 38 and 19 Mev α -particle bombardments of ytterbium by $\underline{\alpha}$, $\underline{\alpha}$ reactions or by growth from an undetected possibly short lived hafnium limit, the possibilities for allocation to mass 172 only. Since the lutecium fraction from 19 Mev α -particle bombardment has a high yield of the 4.0 hour activity, the existence of a short lived hafnium parent is fairly certain, since at this bombarding energy, the $\underline{\alpha}$, $\underline{\alpha}$, $\underline{\alpha}$ reactions necessary to form the 4.0 hour activity directly would either not occur or would in very low yield.

At mass 172 therefore must be placed the 500 day activity decaying by orbital electron capture and the two independent positron emitting activities of half lives 4.0 hour and 3.4 days. Whilst the latter has been separated from a hafnium parent

activity, the 4.0 hour activity was not observed to grow in the hafnium fractions. The 500 day activity has been shown to grow from a hafnium parent but no direct relationship has been established.

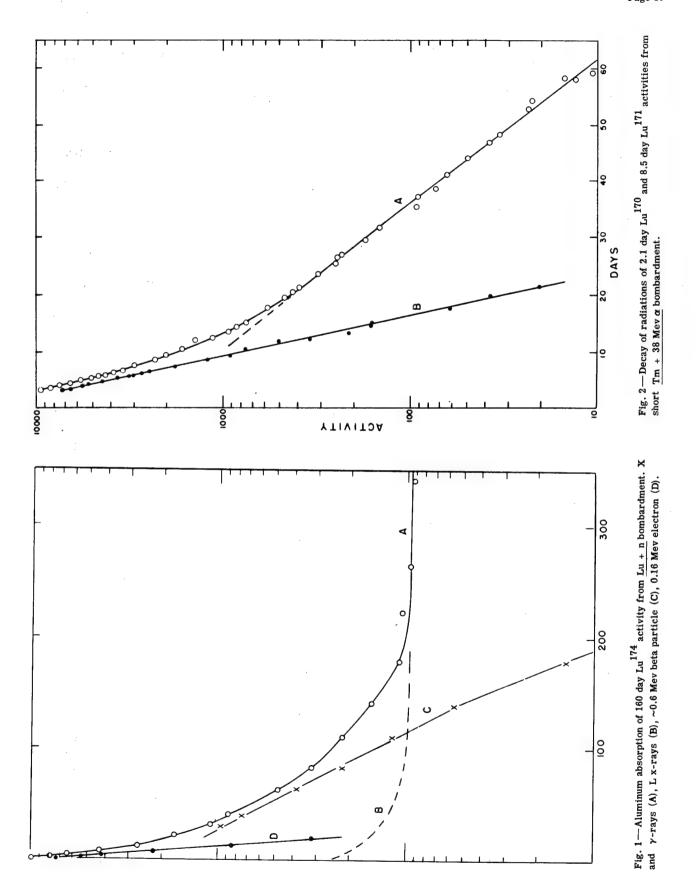
The 6.7 day lutecium activity, whose daughter relationship to a five year hafnium parent has been definitely established is allocated to mass 173. While the complete resolution of this activity from Yb + p bombardments has proved impossible due to the formation of the 8.5 day Lu¹⁷¹ in approximately equal yields, the decays and absorptions of the lutecium fraction provide adequate evidence for a mixture of the 6.7 day and 8.5 day activities, and hence allocation to mass 173 appears not unreasonable.

As has been pointed out previously, the formation of the 67 day Hf¹⁷⁵ in all bombardments of ytterbium with a-particles complicates the characterization of the parent of the 3.4 day lutecium activity. The formation of the 22.0 hour hafnium in both 38 and 19 Mev bombardments eliminates the possibility that this isotope has mass less than 172; since no short lived daughter has been found allocation can be made only to masses 172 or 173. The isotope may be an isomer of Hf¹⁷² or Hf¹⁷³ decaying by either internal transition, or independently by orbital electron capture. The growth of the 6.7 day lutecium from the 22 hour activity would have been observed with the activities of the latter available so that allocation to mass 172 is more probable.

Acknowledgements

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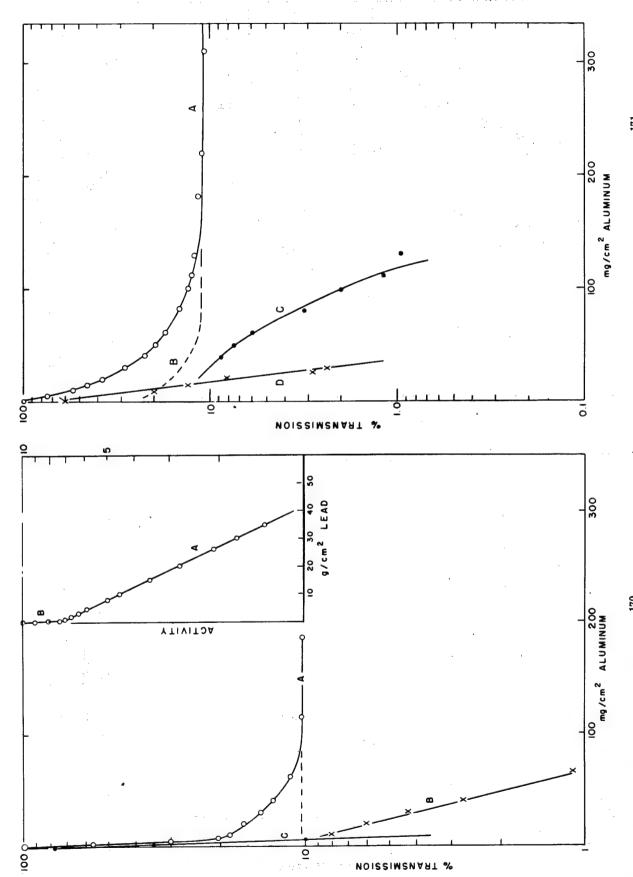
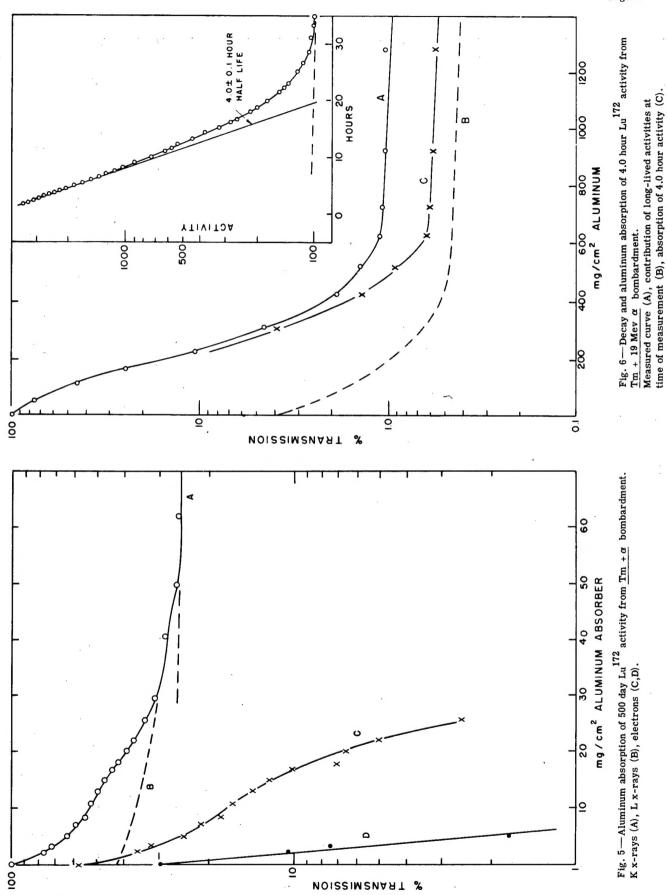
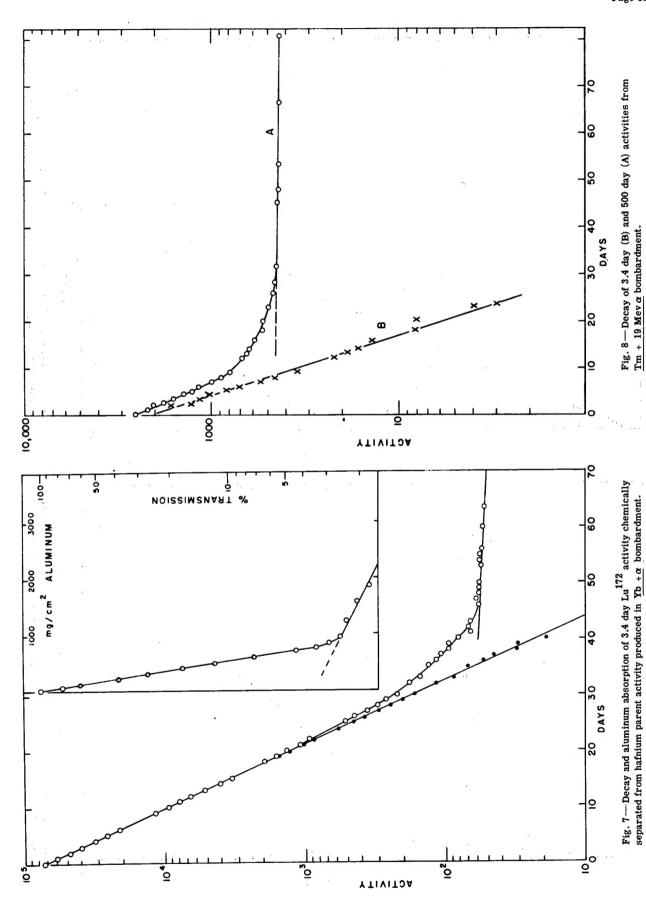


Fig. 3—Aluminum and lead absorptions of 2.1 day Lu¹⁷⁰ from $\frac{Tm + 38 \text{ Mev } \alpha}{c}$ bombarcanent. Aluminum absorption: X and y-rays (A), L x-rays (B), electron (C). Lead absorption: ~2.5 Mev y-ray (A), K x-rays (B).

Fig. 4—Aluminum absorption of 8.5 day Lu 171 activity. X and γ -rays (A), L x-rays (B), electrons (C,D).

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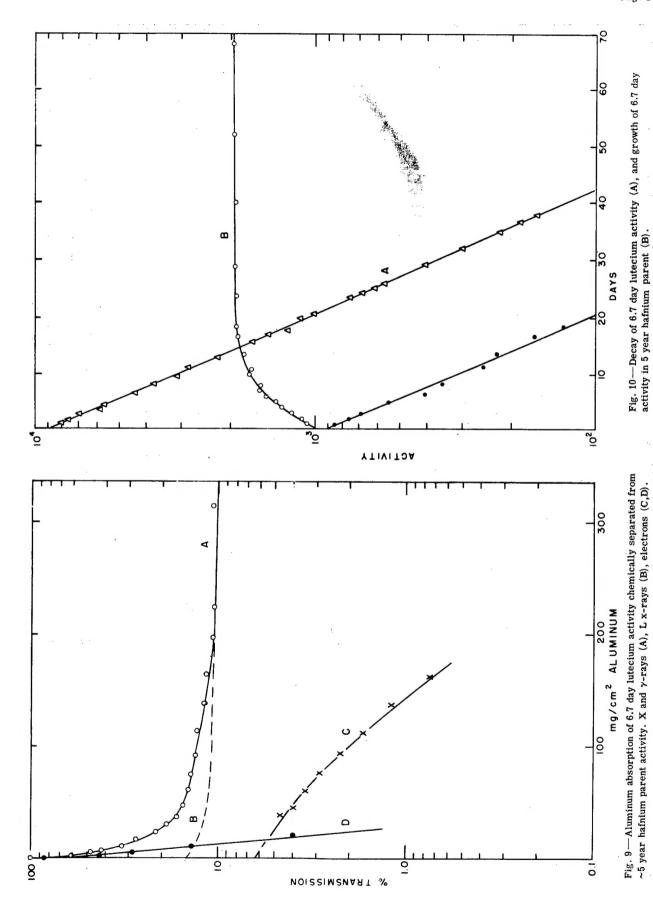




Fig. 12—Decay and aluminum absorption of radiations of 22 hour hafnium activity from $\overline{Yb} + \alpha$ bombardment. X and γ -rays $\overline{(A)}$, \overline{L} x-rays $\overline{(B)}$, electrons $\overline{(C,D)}$.

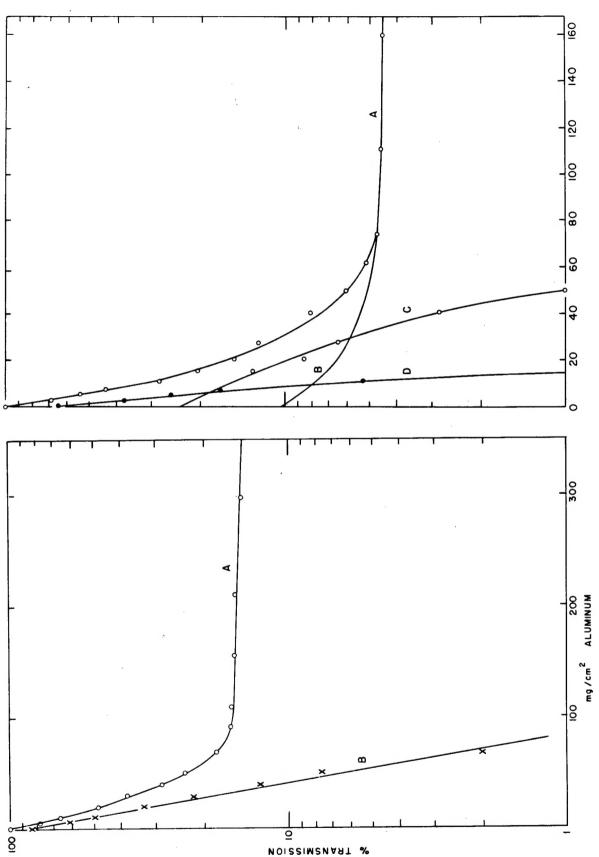


Fig. 11—Aluminum absorption of~5 year hafnium activity from $\frac{Ta+d}{a}$ bombardment. X and γ -rays (A), L x-rays (B) half thickness 15 mg/cm² aluminum.